

PATENT SPECIFICATION

899,284

NO DRAWINGS.

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Date of filing Complete Specification : Oct. 24, 1958.

Application Date : Nov. 1, 1957. No. 34108/57.

Complete Specification Published : June 20, 1962.

Index at Acceptance :—Class 2(2), A3C.

International Classification :—C08b.

COMPLETE SPECIFICATION.

Improved Phosphorylated Cellulose and Method of Obtaining it.

We, UNITED KINGDOM ATOMIC ENERGY AUTHORITY, London, a British Authority, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with an improved phosphorylated cellulose.

The present invention provides a phosphorylated cellulose of improved properties, particularly in its improved suitability for use in the adsorption of thorium from acidic aqueous solutions containing phosphoric acid such as those solutions obtained when monazite is treated with an aqueous acid.

According to the invention, cellulose is phosphorylated by treatment with phosphoric acid containing an excess of a basic nitrogen-containing compound, employing a curing time such that substantially all the phosphorus in the phosphorylating agent employed becomes chemically combined with the cellulose; the phosphorylated cellulose in salt form thus obtained is converted, by treatment with a water soluble acid, from salt form to hydrogen form; the hydrogen-form material is then washed with water to free it from the acid employed to effect the conversion to the hydrogen form; and the water-washed hydrogen-form product is then allowed to stand in contact with water.

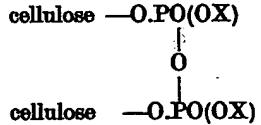
How the invention can be performed will be apparent from the following:—

35 Preparation of Phosphorylated Cellulose in Salt Form.

In the known method of preparing phosphorylated cellulose in salt form (the subject

[Price 4s. 6d.]

of Patent 838,973) cellulose impregnated with phosphorylating agent (phosphoric acid and an excess of a basic-nitrogen-containing compound, for example urea) is heated or "cured" to cause replacement of a proportion of the hydroxyl groups of the anhydro-glucose units of cellulose (usually at least one-third of a hydroxyl group, and sometimes as much as 1.5 or even more hydroxyl groups, per anhydro-glucose unit) by the group $-\text{O.PO(OH)}(\text{OX})$, or the group $-\text{O.PO}(\text{OX})_2$, where X represents the salt-forming group, for instance the ammonium radical, which is formed by breakdown of urea phosphate. In the case of the former group, cross-linking may occur giving a material of the type:—



The rate of the replacement depends on a number of variables, for instance the concentration of the phosphorylating agent in the impregnated cellulose subjected to heating, and in particular it varies directly with the heating temperature employed. However, with any given set of conditions, the progress of the replacement reaction can be followed by stopping the heating, washing the product thoroughly with water to remove unreacted phosphorylating agent, and determining by known means the amount of recovered anhydronium phosphate in the washings. Hence, and from a knowledge of the amount of phosphorylating agent originally present in the impregnated cellulose subjected to

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heating, the extent to which phosphorylation has progressed towards the maximum possible can be calculated. The maximum possible of course depends on the actual proportion of phosphorus : cellulose in the impregnated material subjected to heating.

The first stage in the method of this invention consists in preparing phosphorylated cellulose in salt form by the known method, employing a time of curing such that substantially all the phosphorus (that is, at least 97%) in the phosphorylating agent employed becomes chemically combined with the cellulose. As can be inferred from the description earlier, it is impossible to define the time of curing in absolute units, because the time required depends on many variables. However, as explained above, the progress of the phosphorylation reaction can be followed in any given instance by a simple testing procedure, and hence the curing time required in any given instance can be simply found.

Preferably, the time of curing employed is at least 20% in excess of that required to cause substantially complete combination with cellulose of the phosphorus in the phosphorylating agent employed. The resulting material, which can conveniently be referred to as "over-cured," when subjected to the succeeding stages of the method of the invention, gives a final phosphorylated product of enhanced usefulness, as will appear later.

It is also preferred to carry out the curing procedure with the use of a stream of air, pre-heated to the curing temperature employed, which is forced over the surface of the material to be cured. The employment of this pre-heated forced air stream very materially reduces the time required for the attainment of cure.

Conversion of Phosphorylated Cellulose from Salt Form to Hydrogen Form.

The phosphorylated cellulose in salt form obtained as described above is mechanically broken down, as with a homogeniser, to an appropriate fibre length, and is then treated with a slight excess of a dilute aqueous acid, most conveniently hydrochloric, sulphuric or nitric acid, to replace the salt groups by hydrogen atoms. This operation is conveniently carried out by placing the phosphorylated cellulose in salt form in a column and passing the aqueous acid through it.

If appreciable excess acid is allowed to remain unduly long in contact with the phosphorylated cellulose converted to hydrogen form, it causes some loss of bound phosphoryl groups by fission of their ester linkage with the hydroxyl oxygen of the monosaccharide units of the cellulose. Accordingly, the phosphorylated cellulose in hydrogen form is washed with water until the

washings are substantially free generally speaking, when their pH has risen above 3 (they can be regarded as substantially free) from the acid employed to effect conversion to the hydrogen form.

Allowing the Water-Washed Phosphorylated Cellulose in Hydrogen Form to Stand in Contact with Water. 70

When the water-washed hydrogen-form product is allowed to stand in contact with water there occurs a gradual improvement in the usefulness of the product as an adsorbent for thorium from acidic aqueous solutions containing phosphoric acid; this improvement is in fact detectable within two or three hours of standing with water. The rate of improvement can be accelerated by increasing the temperature of the water with which the phosphorylated cellulose in hydrogen form is allowed to stand in contact, but there is normally nothing to be gained by the use of temperatures above about 30° C. because there is then a considerable tendency for fission of the cellulose-phosphate linkages to occur.

The invention is illustrated by the following example:—

EXAMPLE.

Strips of wood-pulp cellulose (each weighing 10 grams) were totally immersed for one minute in an aqueous solution containing 50% by weight of urea and 18% by weight (as H_3PO_4) of phosphoric acid. The strips were then removed, and the surplus solution was squeezed from them until the ratio weight of liquor adsorbed : weight of cellulose taken had fallen to 3.0. The strips were then placed on trays of stainless steel gauze in an oven electrically heated to 130° C., and air pre-heated to 130° C. was forced through the oven, over the strip surfaces, at a rate such that the oven atmosphere was changed 22 times per minute. After 2½ hours of curing in this manner (representing about 45% over-cure), the strips of phosphorylated cellulose in mono-ammonium form, now rigid and 110 tough, and substantially free from water-115 elutable phosphate, were removed from the oven, immersed in distilled water, and broken down into fibres in a homogeniser. The resultant macerated pulp was filtered in a 115 basket centrifuge, thoroughly washed with large quantities of distilled water to remove water-soluble impurities derived from urea, and spin-dried to a moisture content of 52%. An oven-dried (110° C.) sample of the fibrous 120 product was found to contain phosphorus equivalent to 33.0% PC_4 .

The spin-dried material was made into an aqueous slurry, and transferred to a glass "ion-exchange" column, and washed with 125 an excess of 2N aqueous sulphuric acid to replace the ammonium groups by hydrogen

atoms. The material in the column was then washed with an excess of distilled water until the pH of the effluent liquid had risen above 4. Washing was then stopped and the material was allowed to stand, immersed in the water in the column, for three days. The equivalent phosphate content of the product was 29.7% by weight based on the weight of the corresponding mono-ammonium form. The product can if desired be converted to the mono-ammonium form and oven-dried at 80° C. for storage.

WHAT WE CLAIM IS:—

1. An improved phosphorylated cellulose obtained by treating cellulose with phosphoric acid containing an excess of a basic nitrogen-containing compound employing a curing time such that substantially all the phosphorus in the phosphorylating agent employed becomes chemically combined with the cellulose; converting the material thus obtained from the salt form thus obtained to the hydrogen form by treatment with a water soluble acid; washing the hydrogen-form material with water to free it from said acid; and allowing the water-washed hydrogen-form product to stand in contact with water.

2. An improved phosphorylated cellulose according to Claim 1, obtained employing a curing time at least 20% in excess of that required to cause substantially complete combination with cellulose of the phosphorus in the phosphorylating agent employed. 30

3. An improved phosphorylated cellulose according to Claim 1 or 2, obtained by phosphorylating cellulose with an agent in which the basic-nitrogen-containing constituent is urea. 35

4. A method of obtaining an improved phosphorylated cellulose as set forth in Claim 1, 2 or 3, in which the curing procedure is carried out with the use of a stream of air, pre-heated to the curing temperature employed, which is forced over the surface of the cellulosic material to be cured. 40

5. An improved phosphorylated cellulose obtained substantially as hereinbefore described. 45

6. An improved phosphorylated cellulose obtained substantially as hereinbefore described with reference to the example. 50

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Agent for the Applicants.

PROVISIONAL SPECIFICATION.

Improved Phosphorylated Cellulose and Method of Obtaining it.

We, UNITED KINGDOM ATOMIC ENERGY AUTHORITY, of London, a British Authority, do hereby declare this invention to be described in the following statement:—

This invention is concerned with a method of obtaining phosphorylated cellulose in a form having improved suitability for use in the adsorption of thorium cations from aqueous solution.

In the course of earlier research, it has been shown that phosphorylated cellulose has the property of adsorbing certain metallic cations from acidic aqueous solution of concentration one-tenth normal (N/10) or more with respect to mineral acid, and that the metallic ions thus adsorbed can be recovered by treating the phosphorylated cellulose with an aqueous eluant. However, as subsequent investigations have shown, phosphorylated cellulose as ordinarily available has relatively poor selectivity in the adsorption of "pure" thorium cations from acidic aqueous solutions containing phosphoric acid. For instance, when employed in the treatment of aqueous sulphuric acid extracts of monazite, phosphorylated cellulose as ordinarily available adsorbs thorium in the form of a complex thorium phosphate cation, perhaps $[\text{Th}(\text{H}_2\text{PO}_4)_4]^{4-}$; and when the material

is subsequently treated with an eluting agent for the adsorbed thorium there is simultaneously eluted a high proportion of the adsorbed phosphate, whose presence in the resulting eluate considerably complicates subsequent recovery of the thorium. 85

The present invention is concerned with a method of obtaining a phosphorylated cellulose of improved suitability for use in the adsorption of thorium cations from acidic aqueous solutions containing phosphoric acid. 90

In the method of the invention, cellulose is phosphorylated employing a curing time such that substantially all the phosphorus in the phosphorylating agent employed becomes chemically combined with the cellulose; the phosphorylated cellulose thus obtained is converted, by treatment with acid, from salt form to hydrogen form; the hydrogen-form material is then washed with water to free it from the acid employed to effect the conversion to the hydrogen form; and the water-washed hydrogen-form product is then allowed to stand in contact with water. 95 100 105

How the invention can be performed will be apparent from the following.

*Preparation of Phosphorylated Cellulose
in Salt Form.*

In the known method of preparing phos-

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5 phosphorylated cellulose in salt form, cellulose impregnated with phosphorylating agent (phosphoric acid and an excess of a basic-nitrogen-containing compound, for example 10 urea) is heated or "cured" to cause replacement of a proportion of the hydroxyl groups of the monosaccharide units of cellulose (usually at least one-third of a hydroxyl group, and sometimes as much as 1.5 or even 15 more hydroxyl groups, per monosaccharide unit) by the group $-O.PO(OH)(OX)$, where X represents the salt-forming group, for instance the ammonium radical, which is formed by breakdown of urea phosphate. 20 The rate of this replacement depends on a number of variables, for instance the concentration of the phosphorylating agent in the impregnated cellulose subjected to heating, and in particular it varies directly with 25 the heating temperature employed. However, with any given set of conditions, the progress of the replacement reaction can be followed by stopping the heating, washing the product thoroughly with water to remove unreacted 30 phosphorylating agent, and determining by known means the amount of recovered and hence unconsumed phosphate in the washings. Hence, and from a knowledge of the amount 35 of phosphorylating agent originally present in the impregnated cellulose subjected to heating, the extent to which phosphorylation has progressed towards the maximum possible can be calculated. The maximum possible of course depends on the actual proportion of phosphorus : cellulose in the 40 impregnated material subjected to heating.

The first stage in the method of this invention consists in preparing phosphorylated cellulose in salt form by the known method, 45 employing a time of curing such that substantially all the phosphorus (that is, at least 97%) in the phosphorylating agent employed becomes chemically combined with the cellulose. As can be inferred from the description earlier, it is impossible to define the 50 time of curing in absolute units, because the time required depends on many variables. However, as explained above, the progress of the phosphorylation reaction can be followed in any given instance by a simple testing procedure, and hence the curing time required in any given instance can be simply found.

55 Preferably, the time of curing employed is at least 20% in excess of that required to cause substantially complete combination with cellulose of the phosphorus in the phosphorylating agent employed. The resulting material, which can conveniently be referred 60 to as "over-cured," when subjected to the succeeding stages of the method of the invention, gives a final phosphorylated product of enhanced usefulness, as will appear later.

65 It is also preferred to carry out the curing procedure with the use of a stream of air,

pre-heated to the curing temperature employed, which is forced over the surface of the material to be cured. The employment of this pre-heated forced air stream very materially reduces the time required for the 70 attainment of cure.

Conversion of Phosphorylated Cellulose from Salt Form to Hydrogen Form.

The phosphorylated cellulose in salt form obtained as described above is mechanically broken down, as with a homogeniser, to an appropriate fibre length, and is then treated with a slight excess of a dilute aqueous acid, most conveniently hydrochloric, sulphuric or nitric acid, to replace the salt groups by hydrogen atoms. This operation is conveniently carried out by placing the phosphorylated cellulose in salt form in a column and passing the aqueous acid through it.

If appreciable excess acid is allowed to remain unduly long in contact with the phosphorylated cellulose converted to hydrogen form, it causes some loss of bound phosphoryl groups by fission of their ester linkage with the hydroxyl oxygen of the monosaccharide units of the cellulose. Accordingly, the phosphorylated cellulose in hydrogen form is washed with water until the washings are substantially free (generally speaking, when their pH has risen above 3 they can be regarded as substantially free) from the acid employed to effect conversion to the hydrogen form.

Allowing the Water-Washed Phosphorylated Cellulose in Hydrogen Form to Stand 100 in Contact with Water.

When the water-washed hydrogen-form product is allowed to stand in contact with water there occurs a gradual improvement in the usefulness of the product as an adsorbent 105 for thorium from acidic aqueous solutions containing phosphoric acid; this improvement is in fact detectable within two or three hours of standing with water. The rate of improvement can be accelerated by increasing 110 the temperature of the water with which the phosphorylated cellulose in hydrogen form is allowed to stand in contact, but there is normally nothing to be gained by the use of temperatures above about 30° C. because 115 there is then a considerable tendency for fission of the cellulose-phosphate linkages to occur.

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was squeezed from them until the ratio weight of liquor adsorbed : weight of cellulose taken had fallen to 3.0. The strips were then placed on trays of stainless steel gauze 5 in an oven electrically heated to 130° C., and air pre-heated to 130° C. was forced through the oven, over the strip surfaces, at a rate such that the oven atmosphere was changed 10 22 times per minute. After 2½ hours of curing in this manner (representing about 15 45% over-cure), the strips of phosphorylated cellulose in mono-ammonium form, now rigid and tough, and substantially free from water-soluble phosphate, were removed from the oven, immersed in distilled water, and broken down into fibres in a homogeniser. The resultant macerated pulp was filtered in a basket centrifuge, thoroughly washed with 20 large quantities of distilled water to remove water-soluble impurities derived from urea, and spin-dried to a moisture content of 52%. An oven-dried (110° C.) sample of the fibrous product was found to contain phosphorus equivalent to 33.0% PO₄.

The spin-dried material was made into an aqueous slurry, and transferred to a glass "ion-exchange" column, and washed with an excess of 2N aqueous sulphuric acid to replace the ammonium groups by hydrogen atoms. The material in the column was then 25 washed with an excess of distilled water until the pH of the effluent liquid had risen above 4. Washing was then stopped and the material was allowed to stand, immersed in the water in the column, for three days. The equivalent phosphate content of the product was 29.7% by weight based on the weight of the corresponding mono-ammonium form. The product can if desired be converted to the mono-ammonium form and oven-dried 30 35 40 at 80° C. for storage.

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Abingdon : Printed for Her Majesty's Stationery Office, by Burgess & Son (Abingdon), Ltd.—1962.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2,
from which copies may be obtained.